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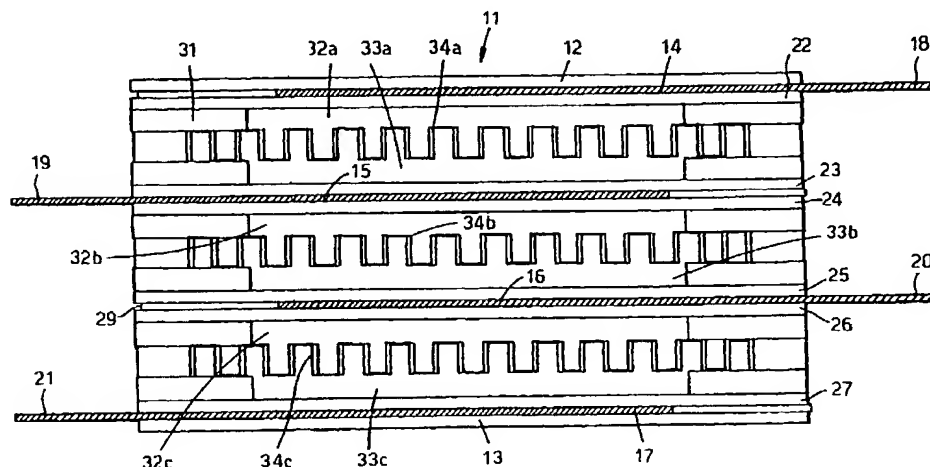
(57) Abstract: Hydrogen is generated from hydrocarbon fuel by a reforming reaction in a reactor (11) in which gaseous hydrocarbon and reforming reaction agents are subjected to the formation of a plasma having an electric field strength within the plasma exceeding 10,000 volts per centimetre, preferably at least 20,000 volts/cm, more preferably at least 40,000 volts/cm or even 80,000 volts/cm. The apparatus has electrodes (14, 15, 16) and dielectric material (22-27), the configuration of which allows for plasma having the electric field strength defined above.

MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

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Production of Hydrogen

The invention relates to the production of hydrogen from hydrocarbon fuel in a process which makes use of a
5   non-thermal plasma reactor.

Fuel cells consuming hydrogen and oxygen offer the promise of providing clean power for motor vehicles. However, this leads to a requirement for an efficient and
10   correspondingly clean process for the production of hydrogen. Ideally this should come, at least initially, from hydrocarbons such as are made available in quantities and on an appropriately wide distribution network in the form of gasoline or diesel for internal
15   combustion engines.

The main routes known for the production of hydrogen from hydrocarbons are steam reforming, partial oxidation and carbon dioxide reforming.
20

Steam reforming involves reaction with water in the form of steam, sometimes referred to as "water shift" and may be represented as

25        $C_mH_n + m\ H_2O \Rightarrow m\ CO + (n/2 + m)\ H_2$, or

          $C_mH_n + 2m\ H_2O \Rightarrow m\ CO_2 + (n/2 + 2m)\ H_2$,
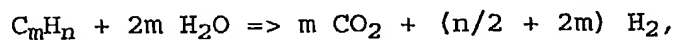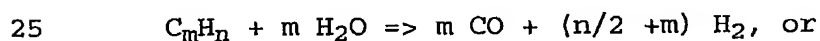
where m and n are the numbers of carbon and hydrogen
30   atoms in a hydrocarbon molecule. These reactions are endothermic and heat energy must be provided to the gaseous reactants to satisfy thermodynamic constraints.
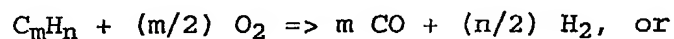
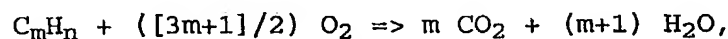A reverse water shift reaction can also take place
35

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$$CO + H_2O \Rightarrow CO_2 + H_2$$
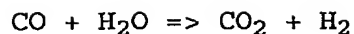
and this reaction is quasi-athermic.
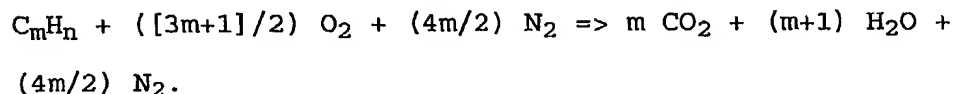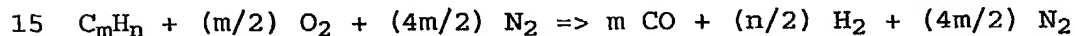
5   In partial oxidation, reaction conditions have to be set up for a hydrocarbon to react with oxygen according to the equations

$$C_mH_n + (m/2) \; O_2 \Rightarrow m \; CO + (n/2) \; H_2, \; or$$

10

$$C_mH_n + ([3m+1]/2) \; O_2 \Rightarrow m \; CO_2 + (m+1) \; H_2O,$$

or with air

15   $$C_mH_n + (m/2) \; O_2 + (4m/2) \; N_2 \Rightarrow m \; CO + (n/2) \; H_2 + (4m/2) \; N_2$$

$$C_mH_n + ([3m+1]/2) \; O_2 + (4m/2) \; N_2 \Rightarrow m \; CO_2 + (m+1) \; H_2O +$$

$$(4m/2) \; N_2.$$

20   The partial oxidation reactions are highly exothermic, and so it is possible to use them in modes where less energy is required compared to steam reforming, thus minimising the power requirements. It also, of course, eliminates the need for water.

25

     Carbon dioxide reforming is used to produce process gas with varying H_2:CO ratios and involves reaction of hydrocarbons with CO_2 (rather than with water)

30      $$C_mH_n + mCO_2 \Rightarrow 2m \; CO + (n/2) \; H_2.$$
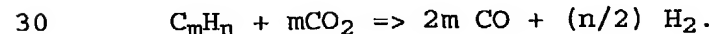
     This reaction is endothermic so that heat must be supplied.

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Apparatus and processes for performing hydrocarbon reforming reactions with assistance from plasma, both thermal and non-thermal have been described in a number of publications, examples of which are patent

5   specification WO 98/28223, SAE Paper No. 982427, October 1998; Int.J.Hydrogen Energy 23,1109, 1998, patent specifications US 5993761, US 6007742, WO 01/00310, WO 01/09031, WO 01/14702.

10   In all these prior art examples, however, the plasma used can only supply a fraction of the energy required to achieve an efficient level of reforming and it is necessary to provide heating to supply at least 80% and more typically 90% or more of the total energy input

15   required. There are a number of disadvantages to these prior art examples. The reactors must be built to operate at elevated temperatures and the materials used in their construction must have suitable mechanical properties for these elevated temperatures. The reaction

20   chambers must be insulated to minimise heat losses. Burners or heat exchangers must be incorporated, adding to the complexity of the devices. There will be a period of time after turn-on over which hydrogen yields and power conversion efficiencies gradually increase from

25   initially low levels to their final levels as the reactor warms up. Change of reactor output will be slow as the thermal response of a reactor will be long. Thus there are requirements for improved apparatus for the plasma-reforming of hydrocarbons.

30

It is an object of the present invention to reduce and, if possible, eliminate the need to supply additional heat energy.

35   According to the invention there is provided an apparatus for performing hydrocarbon reforming reactions,

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which apparatus comprises a reactor chamber having an
inlet duct for feeding gaseous reagents to the chamber
and an outlet duct for reaction products, and, within the
chamber, electrodes and dielectric material, a source of
5   electrical potential connected in use of the apparatus to
apply an electrical potential across the electrodes, the
spacing and configuration of the electrodes and the
dielectric material in relation to the applied electrical
potential in use being such as to generate plasma in
10   gaseous reagents passing through the reactor, in which
plasma the electric field strength is in excess of 10,000
volts per centimetre, preferably at least 20,000
volts/cm, more preferably at least 40,000 volts/cm, and
may desirably be at least 80,000 volts/cm.   .
15

       To achieve such high electric field strengths within
the plasma, the reactor is preferably a dielectric
barrier (or so called "silent discharge") reactor having
at least one electrode with a dielectric barrier layer in
20   intimate contact with its surface or surfaces which face
the other electrode, and the spacing between the
electrodes is sufficiently small for the applied
potential across them to generate plasma having the
aforesaid electric field strength. The reactor may be
25   provided with a plurality of electrodes arranged in pairs
and electrical potential is applied across each pair.
Conveniently, all such electrodes are coated with a
dielectric barrier layer.

30   In an alternative arrangement a bed of high
permittivity dielectric particles fills the space between
electrically conducting surfaces of the electrodes, the
permittivity of the particles serving to concentrate the
electric potential at the contact points between the
35   particles such that the aforesaid electric field strength
is achieved in plasma discharges formed in the

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interstices between the particles.

In a further alternative the electrodes, or each
pair of electrodes, are, or is, provided with a
5   dielectric barrier layer between them and the space
between the electrodes, or each pair of electrodes is
additionally filled with a bed of high permittivity
dielectric particles.

10   We have also found that enhanced formation of
discharge streamers emanating from dielectric surfaces,
is achieved by providing, on those dielectric surfaces
exposed to gas passing through the reactor, an isolated
discontinuous metallic film, preferably less than 10 μm
15   in thickness and not connected to an external source of
electric potential. The discontinuous metallic film may
be in the form of spots or dots of metal and can be
present on one or more of the dielectric barriers. The
metal provides a richer source of electrons than the
20   dielectric material and has the effect of increasing the
number of discharge points emanating from one or more of
the barriers and thereby increasing the efficiency of
treatment of gaseous reagents passing through the
reactor.
25

Alumina is a suitable material for the dielectric
barrier layer although other dielectric ceramic materials
can be used. Barium titanate, calcium titanate or high
permittivity dielectric material including ferroelectric
30   materials are suitable materials for the particles in a
bed reactor. The particles in a bed reactor may be in the
form of spheres, pellets, extrudates, fibres, sheets,
wafers, frits, meshes, coils, foams, honeycomb monoliths
or granules or as a coating on any of the above shapes or
35   contained within a dielectric, polymeric or metallic
material in any of the above shapes or as a combination

of more than one of the aforementioned forms of
particulate material.

Preferably the apparatus includes a membrane
5   positioned to receive output gaseous product from the
reactor chamber to separate hydrogen gas therefrom. The
membrane may be outside the reactor chamber or may be
positioned within the reactor chamber and may be exposed
to the plasma, in which case the plasma may serve to
10 clear any fouling from the membrane. The membrane may
conveniently be provided by one or more of the electrodes
in the reactor chamber, which electrode or electrodes is
or are in the form of a gas permeable electrically
conducting material which itself is permeable to hydrogen
15 but not other reaction products, or in the form of a gas
permeable electrically conducting material having a
coating thereon of material which is permeable to
hydrogen but not other reaction products. Depending upon
its location, the membrane may comprise a ceramic such as
20 zirconia or alumina, or may be polymeric or metallic. The
membrane pore size is preferably less than 2 nanometres.
Location of the membrane within an electric field,
specifically such as the electric field in the plasma,
may enhance the membrane performance. The membrane may be
25 coated with materials, such as metals, for example,
palladium or titanium, or metal oxides which serve to
enhance the separation of hydrogen from other reaction
products, or alternatively or additionally which serve to
store hydrogen.
30

Pressure swing absorption apparatus can be used as
an alternative to membrane processes for hydrogen
separation as indicated in US 5,932,181 (Yukong Limited).
Here the gaseous stream leaving the non-thermal plasma
35 reactor can contain hydrogen, carbon monoxide, carbon
dioxide, water and unreacted hydrocarbon. Gaseous

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components other than hydrogen are absorbed on a bed of
absorbent in the pressure swing absorption apparatus,
such as molecular sieve. Alternative cycles of operation
of the apparatus at atmospheric pressure and vacuum or
5   reduced pressure can selectively absorb gaseous
components other than hydrogen.

Catalytic materials may be incorporated in the
apparatus to assist the desired reforming reactions. Such
10   catalytic materials may be positioned within the plasma
region, or so as to act upon gaseous medium leaving the
reactor chamber. Depending upon the required location,
the catalytic material may be provided separately as
particles in a bed or a coating on a substrate through
15   which the gaseous medium is passed, or in the form of a
coating upon the electrodes, upon the dielectric barrier
material, upon dielectric bed particles, or upon the
membrane. Suitable catalytic materials are nickel,
palladium, platinum, ruthenium or rhodium that can also
20   be supported on an oxide support, preferably rhodium or
platinum on alumina.

The invention includes a method of reforming gaseous
hydrocarbon, which method comprises passing gaseous
25   reactants comprising hydrocarbon together with steam or
carbon dioxide and/or oxygen through a reactor chamber
having an inlet duct for feeding gaseous reagents to the
chamber and an outlet duct for reaction products, and,
within the chamber, electrodes and dielectric material,
30   applying an electrical potential across the electrodes,
the applied electrical potential in relation to the
spacing and configuration of the electrodes and the
dielectric material being such as to generate plasma in
the gaseous reactants passing through the reactor, in
35   which plasma the electric field strength is in excess of
10,000 volts per centimetre, preferably at least 20,000

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volts/cm, more preferably at least 40,000 volts/cm, and
may desirably be at least 80,000 volts/cm.

5   Gaseous hydrocarbons that are to undergo reforming
reactions can be derived from hydrocarbons that are in
the gaseous, liquid or solid state at normal ambient
temperatures.

      Specific constructions of reactor for carrying out
10   the invention will now be described by way of example and
with reference to the drawings filed herewith, in which:

      Figure 1 shows a reactor in cross-section taken
transverse to the direction of incoming and out-flowing
15   gas,

      Figure 2 is a longitudinal section of a second
reactor, and

20   Figure 3 is a schematic view showing the gas flow
path through the reactor of Figure 2.
      A number of known forms of non-thermal plasma
reactor are suitable for carrying out the present
invention. As indicated above, these may be particulate
25   bed reactors having a bed of high permittivity particles
between electrodes of electrically conducting material of
the general type described in, for example, patent
GB2274412. Alternatively, a dielectric barrier reactor
(or so-called "silent discharge" reactor) or a reactor
30   which has both dielectric barrier and a bed of high
permittivity particles may be used. The requirement in
accordance with the invention is to achieve an electric
field strength within the plasma at least in excess of
10,000 volts/cm, preferably significantly higher, even up
35   to and in excess of 80,000 volts/cm. This is achieved by
attention to a combination of characteristics, namely the

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electrical potential applied, the spacing between the
electrodes, the permittivity of the dielectric barrier
and the permittivity of dielectric particles when used in
the reactor.

5

Figure 1 illustrates an adaptation of a dielectric
barrier reactor in which a membrane for separating
hydrogen produced in the reactor from other reaction
products is incorporated within the reactor.

10

Referring to Figure 1, the reactor 11 comprises a
rectangular box enclosure formed between a ceramic cover
plate 12 and a ceramic base plate 13. In this example,
there are four electrode plates 14, 15, 16, and 17, each
15   having an extension to provide an electrical contact,
those, 18, 20, from electrode plates 14, 16 being on one
side of the reactor 11, whilst the electrical contacts
19, 21 from the electrode plates 15, 17 are on the other
side of the reactor 11.

20

Each electrode plate 14, 15, 16, 17 is secured with
adhesive between respective pairs of ceramic plates 12,
22; 23, 24; 25, 26; and 27, 13. Where the electrode
plates finish short of the edges of the ceramic plates,
25   the space between respective ceramic plates is filled
with ceramic adhesive, as for example referenced at 29.
The ceramic plates serve as dielectric barrier layers for
their associated electrode plates. Alumina is a suitable
material for the ceramic dielectric barrier material.
30   Aluminium nitride can also be used.

The dielectric barrier material can be a catalytic
material, or contain a catalytic coating in or on its
surface. The catalytic material can be produced by ion-
35   exchange, doping, depositing by wet chemical techniques
such as sol-gel processing, incipient wetness, by

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sputtering or by chemical vapour deposition or by thermal
spraying for example by plasma spraying or by physical
and chemical vapour deposition.

5   Ceramic spacers, one of which is referenced at 31,
serve to hold the electrode plates spaced apart and also
to form side walls of the rectangular box enclosure. At
each end of the reactor 11, openings are provided at 32a,
32b and 32c for gas flow into and out of the reactor. At
10 the outlet end of the reactor, separate openings are
provided at 33a, 33b, 33c for product hydrogen gas flow
out of the reactor.

        The ceramic spacers (such as 31) are arranged also
15 to support, in each of the three spaces between the four
electrode plates, a layer of membrane 34a, 34b, and 34c,
each of which, in this example, is a sheet comprising a
ceramic such as zirconia or alumina. The membrane pore
size is less than 2 nanometres. The membranes 34a, 34b,
20 and 34c provide a surface which extends along the length
of the respective gas flow path (32a, 32b and 32c).

        These membranes may be in the form of different
shapes in order to optimise the available surface for
25 permeation of hydrogen therethrough. The membranes can
have indentations with a square wave-form as shown in
Figure 1, but other shapes such as indentations with a
triangular form can be used.

30   In operation, the reactor 11 is connected to the
source of gaseous hydrocarbon and appropriate reforming
reagents (steam, carbon dioxide or oxygen, according to
the required reforming reaction) to undergo reforming.
The gaseous reagents flow into the reactor at one end
35 through the openings 32a, 32b, 32c and reaction products
pass out of these openings at the other end of the

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reactor.   Hydrogen formed in the reactor permeates through the membranes 34a, 34b, 34c and exits from the reactor 11 via the openings 33a, 33b, 33c.

5   An electrical power supply (not shown) is connected to apply between the pair of electrode plates 15, 17 and the pair of electrode plates 14, 16 a pulsed or alternating potential or direct current of the order of kilovolts to tens of kilovolts and (in the case of pulsed
10 or alternating potential) repetition frequencies in the range 50 Hz to 50 kHz. The discharge gaps are narrow, that is of the order of 0.5 to 5 millimetres, the dimension transverse to the gap dimension being of the order of 10 to 200 millimetres. The small gap dimension
15 is important in that a practical level of applied voltage can generate a plasma discharge in which the electric field strength has the required magnitude, as explained above. The plasma, together with any catalytic material incorporated in or on the dielectric barrier material,
20 acts to promote the reforming reactions, the plasma providing sufficient energy input to avoid, or at least significantly reduce, the need to supply heat to the reactor.

25   Referring to Figure 2, a second reactor for the plasma assisted reforming of hydrocarbon consists of a reactor chamber 300 which has inlet and outlet stubs 301, 302, respectively, by means of which gaseous reagents are introduced into the reactor and reaction products flow
30 out.

         Inside the reactor chamber 300 there is an inner electrode 303 which is supported within a dielectric tube 304, made for example out of α-alumina which has its
35 upstream end closed by a spherical dome 305 to facilitate the flow of gaseous reagents through the reactor. The

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inner electrode 303 is supported in the dielectric tube
304 by two spider supports 306, 307. The inner surface of
the dielectric tube can be metallised with a metal
coating in order to increase the physical contact between
5   the electrode and dielectric tube. The support 307 is
connected to a high voltage input terminal 308 via a
ceramic insulated feed 309 so that a potential of the
order of kilovolts to tens of kilovolts and repetition
frequencies in the range 50 to 50,000 Hz can be applied
10 to the inner electrode 303. Concentric with the inner
electrode 303 and dielectric tube 304 is a grounded outer
electrode 310 made for example of stainless steel. The
dielectric tube 304 and outer electrode 310 are supported
within the reactor chamber 300 by disks 311, 312 made of
15 an insulating ceramic material, such as alumina. A
compliant heat resistant material 313 is interposed
between the electrode support 311 and the dielectric tube
304.

20   As shown in Figure 3, the outer electrode 310 has a
series of baffles 314 and slots 315 315a. The baffles
314 extend from the outer electrode 310 to the inner
surface of the wall of the reactor chamber 300 and act as
grounding connections as well as causing the gaseous
25 reagents to follow a convoluted path which has both
axial, and circumferential components and being at least
partially helical. There is also a radial component of
flow, initially inwardly as the gaseous reagents transfer
from outside the outer electrode 310 to the space between
30 the electrodes 310 and 303 and then outwardly as the gas
returns to exit from outside the outer electrode 310.
Thus there is also a spiral component in the flow.

The baffle 314 is arranged to divide the space
35 between the electrode 310 and the reactor chamber 300
into six segments. At the gas inlet end three of these

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segments are closed off at 314a, 314b and 314c to axial
gas flow and the remaining three segments are open to
axial gas flow into the space between the electrode 310
and the reactor chamber 300. These latter three segments

5   are closed off by the baffle 314 at the gas outlet end of
the reactor. Consequently the gas is forced to pass via
slot 315 radially into the space between the electrodes
303 and 310 then passing in at least a partially helical
manner before passing radially via the next slot 315a

10 into the next segment of space between electrode 310 and
reactor chamber 300. The baffle 314 leaves open this
segment at the gas outlet end, allowing exhaust of the
gaseous reaction products. Thus it will be seen that the
gases both enter and leave the main part of the reactor

15 300 along the surface of the outer electrode 310 and the
electrode supports 311, 312 have reliefs at their
circumferences which are so positioned as to permit this
to happen. Thus for a given gas velocity, the residence
time of the gaseous reagents in the electric field is

20 increased compared with either purely axial or radial
flow. Note that in Figure 3 part of the electrode 310 has
been shown cut away at 316. This cut away is shown in the
Figure only to illustrate the flow of the gases as they
pass between the electrodes 303 and 310 and does not

25 represent a structural feature of the reactor.

This form of reactor, as shown in Figures 2 and 3
can readily be provided with a bed of particulate high
permittivity material filling the space between the

30 electrode 303 (with its dielectric barrier covering tube
304) and electrode 310. The reactor in this form is then
an illustration of a reactor which has both dielectric
barrier and a bed of high permittivity particles.

35   It will be appreciated that the gaseous products
emerging from the reactor of Figures 2 and 3 will require

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further treatment, as by membrane separation, to separate reaction products from one another, in particular to separate hydrogen from the other reaction products.

5   Use of a series spark gap can enhance the performance of the reactors. The electrical power supply (not shown) applies a discharge potential across the electrode plates 15, 17 and 14, 16 (Figure 1) or between the inner electrode 303 and the grounded outer electrode

10 310 (Figure 2). The operating voltage V_g of a dielectric barrier reactor of capacitance C_2' is practically constant and represents the voltage required to break down the gas gap within the reactor with the formation of charge limited microdischarges. The value of V_g is related to

15 the electric field at the surface of the dielectric barrier (or between dielectric particles or beads if the reactor is packed therewith) and determines the maximum energy that can be given to electrons in the microdischarges.

20

The value of V_g is pretty well determined, once the reactor geometry, packing, and gas operating temperature and pressure have been set.

25   It is possible to bring the reactor voltage V up to the value V_g faster if a series spark gap of capacitance C_1 and breakdown voltage V_t is positioned in the supply line. If dV/dt is fast enough then the gap may overvolt before initiation, producing higher energy electrons in

30 the microdischarge.

The Voltage across the reactor at any instant is:

$$V = V_s (C_1 / (C_1 + C_2))$$

35

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That is, the arrangement operates simply as a capacitative voltage divider.

If the spark gap capacitance is the same as the
5   overall reactor capacitance i.e C1=C2, then V = Vs/2.
Thus the supply voltage Vs would need to reach at least
2Vg before Vg could be attained across the reactor and
microdischarges formed. If the spark gap is arranged to
spark over at Vt, just lower than Vg and before discharge
10 is initiated in the main reactor, then potentially up to
2Vg can be applied very quickly across the reactor
itself. The application speed of this pulse can be
expected to lead to beneficial overvolt conditions in the
formation of the microdischarges, making them more
15 effective.

The reactor will discharge in a few nanoseconds as
the microdischarge runs its course and the voltage across
C1 and C2 will fall switching off the spark gap. Using an
20 AC power supply automatically repeats the cycle by
recharging the 'reactor + series spark gap' to a new and
slightly higher level as the AC voltage slowly
increments. The voltage level has to be slightly higher
for discharges subsequent to the first, because the
25 capacitance C2 then has a base charge which has to be
overcome.

It is envisaged that, instead of a spark gap and a
reactor in series, one might use two dielectric barrier
30 reactors in series, one with a large gap and the second
with a smaller gap to fulfil the functions of C1 and C2
above.

The invention is not restricted to the details of
35 the foregoing example(s). For instance additional energy,
if required, can be supplied to the plasma by coupling

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microwave energy into the reactor chamber.

As mentioned above, enhanced formation of discharge
streamers emanating from dielectric surfaces is achieved
5   by providing on those surfaces exposed to gas an isolated
discontinuous metallic film, preferably less than 10 μm
in thickness and not connected to an external source of
electric potential. The discontinuous metallic film may
be in the form of spots or dots (of any circumferential
10   shape, such as circular, rectangular or irregular, even
fractal) of metal and can be present on one or more of
the dielectric barriers. Such added metallic sources of
discharge points can also be provided on or in high
permittivity dielectric particles, where these are also
15   provided in the gas flow path between the electrodes.
Thus, for example such high dielectric packing material
particles in the form of spheres or other shapes may be
provided with surface deposits of thin film metal dots or
spots. Alternatively, the packing itself may contain a
20   distribution of metallic spheres (or other shapes) in
amongst the dielectric particles.

Hydrogen produced in a process that uses a non-
thermal plasma reactor can have many applications. For
25   example in chemical synthesis, such as in Fischer-Tropsch
reactions, in catalytic reactions both heterogeneous and
liquid-phase catalysis, hydrogenation reactions and the
synthesis of ammonia. The chemical synthesis may take
place in a plasma reactor. It can also be used for the
30   reduction of nitrogen oxides in the gaseous emissions
from internal combustion engines. The hydrogen can be
used as a gaseous source for fuel cells whose electrical
output can be used for powering mobile vehicles on land,
sea, air or in space such as cars, lorries, trains, ships
35   aircraft and satellites as examples or for supplying
electricity to stationary objects such as domestic

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appliances or for recharging batteries. Additionally, as
a fuel for turbine generators and as a fuel for auxiliary
back-up sources of power or as a fuel for direct
injection into internal combustion engines. The hydrogen
5 can be used in oil refinery applications for example to
alter the octane levels of the products during refining
of crude oils. Hydrogen and carbon monoxide in the
product stream from a plasma reactor for the reforming of
hydrocarbons can be used hydroformylation reactions for
10 example the hydroformylation of alkenes that can be
derived from refining operations. The hydrogen can also
be contained in hydrogen-storage systems.

When reforming is carried out on long-chain
15 hydrocarbons rather than short chain molecules such as
methane, addition of hydrogen to the reactant entering
the plasma can curtail the formation of polymeric
hydrocarbon species and increase the yield of hydrogen
product. It can be difficult to reform high molecular
20 weight species, for example those found in diesel, by
conventional reforming processes that do not involve the
use of plasmas. A non-thermal plasma reactor can be used
to crack diesel into smaller molecular species that can
then undergo reforming conventionally in the absence of a
25 non-thermal plasma reactor. Partial reforming can also
take place resulting in the production of oxygenated
hydrocarbons.

Other types of non-thermal plasma reactor can be
30 used for the reforming of hydrocarbons. Corona reactors,
an example of which is given in GB 2 282 738 B can be
used. Microwave plasmas for example those generated by
the use of electrodes that concentrate the microwave
radiation into a plasma-forming region as described in GB
35 2 324 196 B can also be used for carrying out reforming
reactions.

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Claims

1.   An apparatus for performing hydrocarbon reforming
reactions, which apparatus comprises a reactor (11;300)
5 having an inlet duct(32a,32b,32c; 301) for feeding
gaseous reagents to the reactor (11;300) and an outlet
duct (33a,33b,33c; 302) for reaction products, and,
within the reactor (11;300), electrodes (14,15,16,17;
303,310) and dielectric material (22-27;304), a source of
10 electrical potential connected in use of the apparatus to
apply an electrical potential across the electrodes
(14,15,16,17; 303,310), characterised in that the spacing
and configuration of the electrodes (14,15,16,17;
303,310) and the dielectric material (22-27;304) in
15 relation to the applied electrical potential in use is
such as to generate plasma in gaseous reagents passing
through the reactor (11;300), in which plasma the
electric field strength is in excess of 10,000 volts per
centimetre.
20

2.   An apparatus as claimed in claim 1, further
characterised in that the electric field strength within
the plasma is at least 20,000 volts per centimetre.

25 3.   An apparatus as claimed in claim 1, further
characterised in that the electric field strength within
the plasma is at least 40,000 volts per centimetre.

4.   An apparatus as claimed in claim 1, further
30 characterised in that the electric field strength within
the plasma is at least 80,000 volts per centimetre.

5.   An apparatus as claimed in any of the preceding
claims, wherein the reactor (11;300) is a dielectric
35 barrier reactor having at least one electrode
(14,15,16,17;303) with a dielectric barrier layer (22-

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27;304) in intimate contact with its surface or surfaces
which face the other electrode, further characterised in
that the spacing between the electrodes (14,15,16,17;
303,310) is sufficiently small for the applied potential
5 across them to generate plasma having the said electric
field strength.

6.   An apparatus as claimed in any of the preceding
claims, further characterised in that the reactor (11) is
10 provided with a plurality of electrodes (14,15,16,17)
arranged in pairs and electrical potential is applied
across each pair of electrodes.

7.   An apparatus as claimed in claim 6, further
15 characterised in that all the electrodes (14,15,16,17)
are coated with a dielectric barrier layer.

8.   An apparatus as claimed in any of claims 1 to 6,
further characterised in that a bed of high permittivity
20 dielectric particles fills the space between electrically
conducting surfaces of the electrodes (14,15,16,17;
303,310), the permittivity of the particles serving to
concentrate the electric potential at the contact points
between the particles such that the aforesaid electric
25 field strength is achieved in plasma discharges formed in
the interstices between the particles.

9.   An apparatus as claimed in any of claims 1 to 7,
wherein the dielectric barrier layer comprises alumina.
30
10. An apparatus as claimed in claim 8, wherein the
particles comprise particles of barium titanate or
calcium titanate or high permittivity dielectric
material.
35
11. An apparatus as claimed in claim 8 or claim 10,

wherein the particles are in the form of spheres,
pellets, extrudates, fibres, sheets, wafers, frits,
meshes, coils, foams, honeycomb monoliths or granules or
as a coating on any of the above shapes or contained
5   within a dielectric, polymeric or metallic material in
any of the above shapes or as a combination of more than
one of the aforementioned forms of particulate material.

12.   An apparatus as claimed in any of the preceding
10   claims, further characterised in that there is included a
membrane positioned to receive output gaseous product
from the reactor (11,300) to separate hydrogen gas
therefrom.

15   13.   An apparatus as claimed in claim 12, further
.characterised in that the membrane is outside the reactor
(11,300).

14.   An apparatus as claimed in claim 12, further
20   characterised in that the membrane (34a,34b,34c) is
positioned within the reactor (11) and is exposed to the
plasma.

15.   An apparatus as claimed in claim 14, further
25   characterised in that the membrane (34a,34b,34c) is
provided by one or more of the electrodes in the reactor
chamber, which electrode or electrodes is or are in the
form of a gas permeable electrically conducting material
which itself is permeable to hydrogen but not other
30   reaction products.

16.   An apparatus as claimed in claim 14, further
characterised in that the membrane(34a,34b,34c) is
provided by one or more of the electrodes in the form of
35   a gas permeable electrically conducting material having a
coating thereon of material which is permeable to

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hydrogen but not other reaction products.

17.   An apparatus as claimed in any of the preceding
claims, wherein catalytic materials are incorporated in
5 the apparatus to assist the desired reforming reactions.

18.   A method of reforming hydrocarbon comprising forming
within a gaseous reaction mixture including the
hydrocarbon a plasma in which the electric field strength
10 exceeds 10,000 volts per centimetre.

19.   A method of reforming hydrocarbon comprising forming
within a gaseous reaction mixture including the
hydrocarbon a plasma in which the electric field strength
15 is at least 20,000 volts per centimetre.

20.   A method of reforming hydrocarbon comprising forming
within a gaseous reaction mixture including the
hydrocarbon a plasma in which the electric field strength
20 is at least 40,000 volts per centimetre.

21.   A method of reforming hydrocarbon comprising forming
within a gaseous reaction mixture including the
hydrocarbon a plasma in which the electric field strength
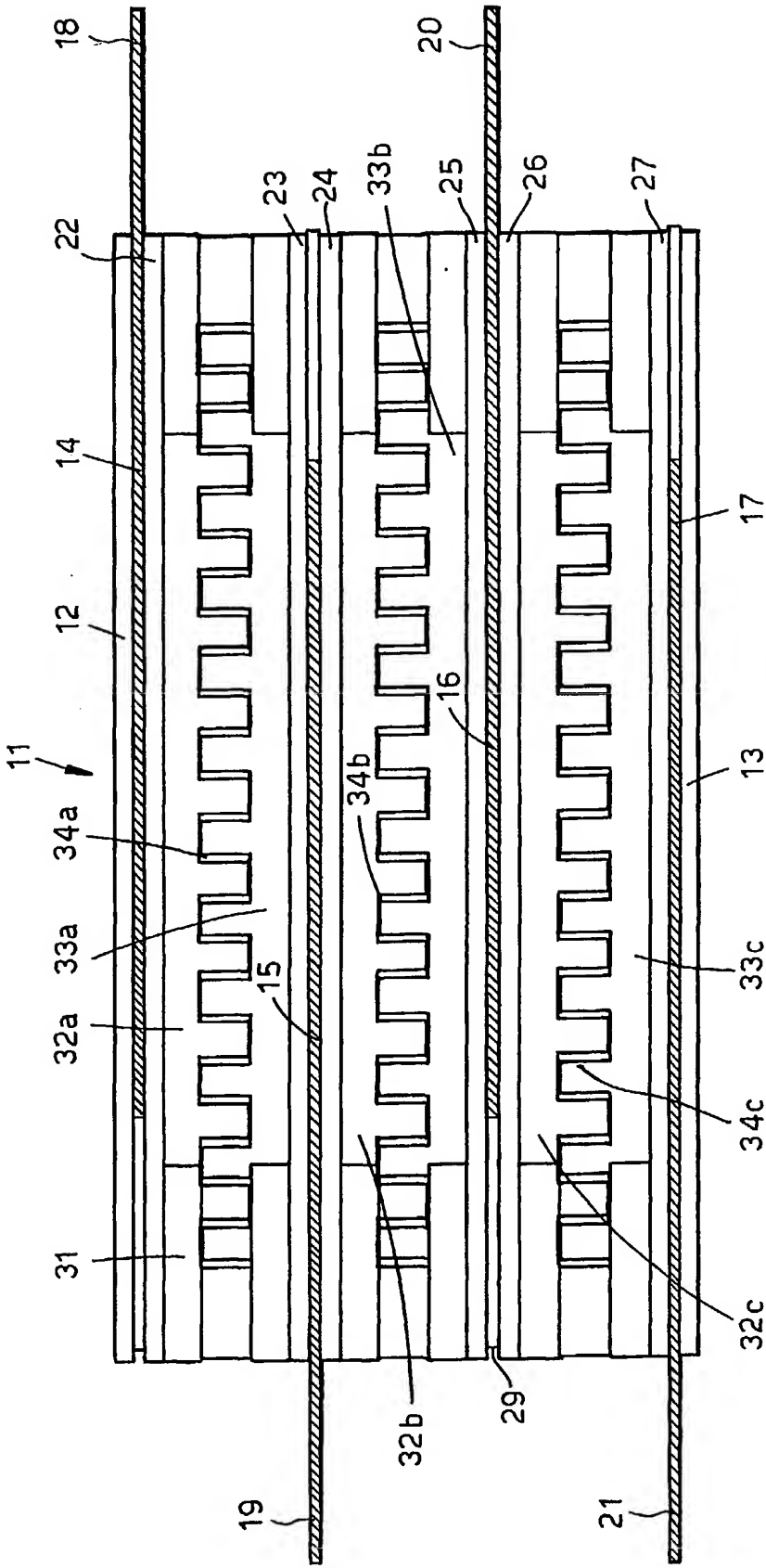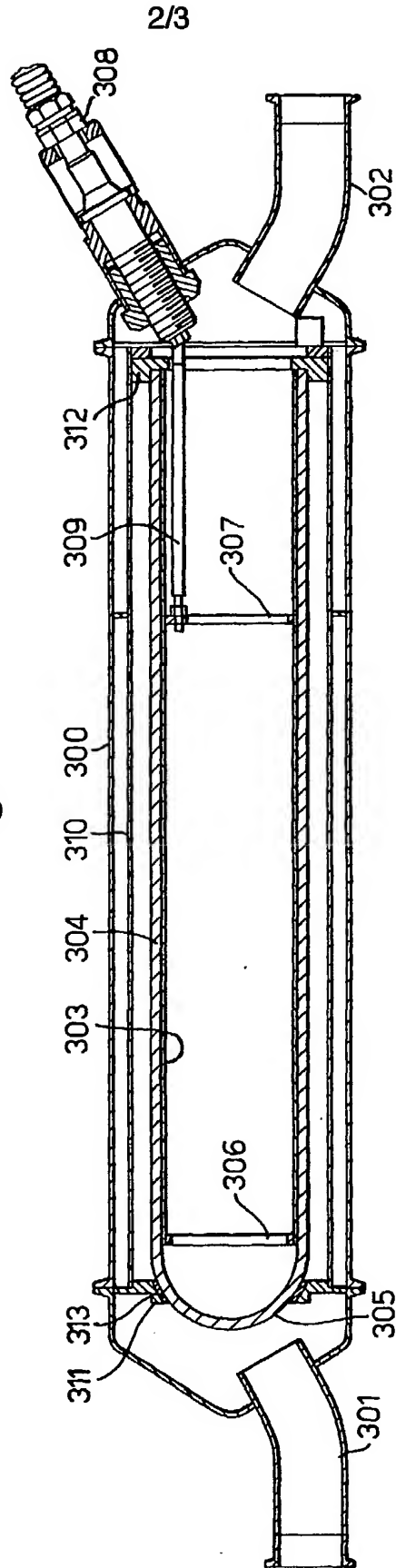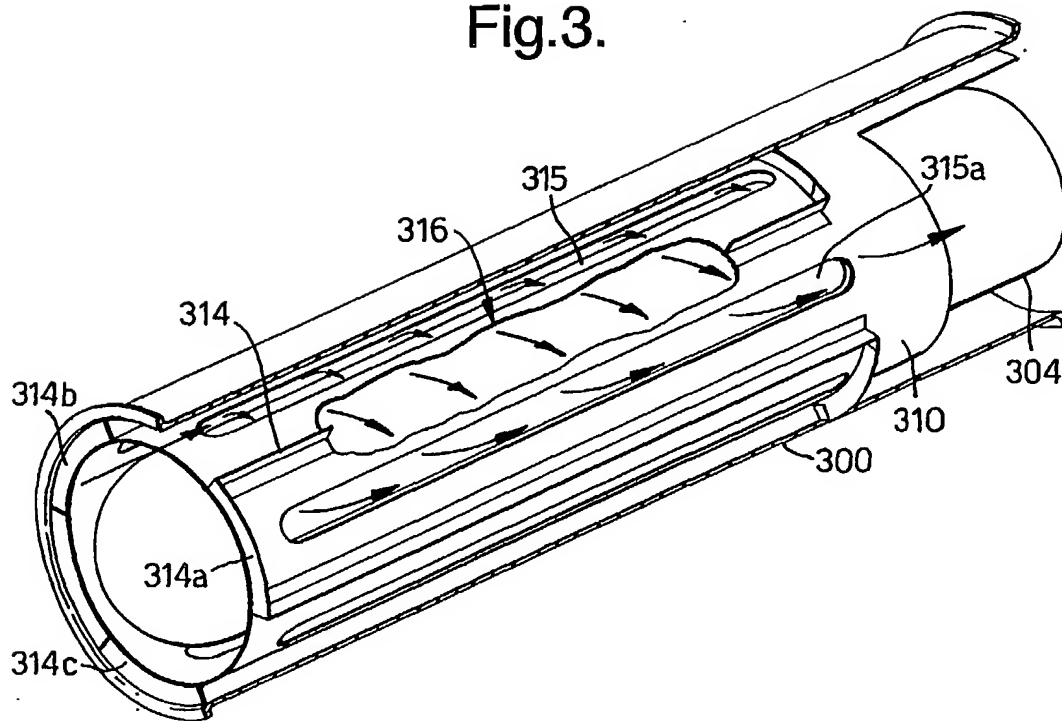25 is at least 80,000 volts per centimetre.

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Fig.1.

Fig.2.

Fig.3.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C01B3/34   B01J19/08   B01J19/24   B01J12/00   C01B3/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C01B   B01J   B01D   F01N   H05H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, EPO—Internal, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 71866 A (ANDREWS PETER JAMES ;MARTIN ANTHONY ROBERT (GB); SHAWCROSS JAMES T) 30 November 2000 (2000-11-30) page 15, line 25 –page 16, line 19 claims; figure 3	1–5,8,9
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X	US 5 746 051 A (KIESER JOERG ET AL) 5 May 1998 (1998-05-05) the whole document	1–5,8,9, 11

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the International search	Date of mailing of the International search report
31 May 2002	07/06/2002

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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